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Conductance and Work Function of TiO_2 Nanotubes Based Gas Sensors

V. Galstyan[a,b,*], E. Comini[b,a], C. Baratto[a,b], M. E. Mazhar[b], A. Ponzoni[a], V. Sberveglieri[a], N. Poli[b], G. Faglia[b,a], G. Sberveglieri[a,b]

[a]*Sensor Lab, CNR, National Institute of Optics (INO), Via Valotti 9, 25133 Brescia, Italy*
[b]*Sensor Lab, Department of Information Engineering, University of Brescia, Via Valotti 9, 25133 Brescia, Italy*

Abstract

We studied growth process of TiO_2 nanotubes and investigated their gas sensing properties using two different approaches such as chemoresistive and Kelwin probe methods. The morphology and the crystal structure of the samples were analyzed using scanning electron microscopy and micro-Raman spectroscopy. Morphological analysis showed that well-aligned and highly ordered nanotubes were obtained by means of electrochemical anodization method. Structural investigations showed the nanotubes were crystallized in the anatase phase after the post-growth annealing. The functional properties of obtained structures were investigated towards different gases in a wide range of operating temperatures.

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Keywords: TiO_2 nanotubes; chemical sensors; work function

1. Introduction

Detection of minor gas leaks, harmful chemical vapors and explosives in environment has been a challenging research problem for many decades as it involves health, safety and environmental risks. However, gas sensor technologies are still developing and have yet to reach their full potential in capabilities and usage.

Wide bandgap semiconducting metal oxides (MOXs) are attractive materials for the detection of explosive, hazardous and toxic gases due to changes in their conductance when oxidizing or reducing species in air chemisorbs

* Corresponding author. Fax: +39-030-209-1271.
E-mail address: vardan.galstyan@unibs.it

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onto their surface [1]. These conductivity changes are exploited for fabrication of conductometric chemical sensors based on MOXs.

Kelvin probe (KP) is another method for the characterization of the sensing properties of MOX materials. KP is a well established method for the measurement of the work function and its variation induced by modifications due the adsorption and desorption of gases on the surface of the MOX nanostructures. This is a relatively facile technique to monitor the variation of the surface potentials during the adsorption and desorption of gases from and to the vapor phase [2,3].

MOX nanotubes (NT) are attractive structures for gas sensing since they provide access to three different contact regions: the tubes' inner and outer surfaces as well as the top side. Especially well-ordered TiO_2 NTs with the large surface area, high chemical activity and porosity have been considered as promised structures for applications in gas sensors [4].

Herein, we report synthesis and gas sensing properties of TiO_2 NTs. We obtained the tubular arrays by means of electrochemical anodization method and post-growth annealing. We investigated gas sensing properties of the structures using two different approaches such as chemoresistive and KP methods.

2. Experimental

TiO_2 NTs were obtained by the electrochemical anodization of metallic Ti thin films at room temperature. Anodization was carried out by potentiostatic mode in the NH_4F and H_2O contained glycerol using a two-electrode configuration. As-prepared samples were crystallized by thermal annealing at 400 °C for 6 h in air. The formation and the growth mechanism of obtained tubular structures were investigated. Obtained nanostructures were analyzed by means of scanning electron microscopy (SEM) and micro-Raman spectroscopy. Gas sensing properties of the NTs were investigated using chemoresistive and KP methods. The chemoresistive measurements were performed by the flow-through method in a thermostatically sealed chamber with controlled temperature and relative humidity. A detailed description of the experimental set-up and the contact geometry we reported in [5]. KP method directly detects the change of the surface work function. The variations in surface contact potential difference were recorded by a commercial probe Besocke Delta Phi, consisting a gold grid of 2 mm in diameter, oscillating very near to the sample surface via piezoelectric transducer with typical frequency of 170 Hz, and controlled by a standard zero-locking Kelvin control system in a 1 L stainless steel closed chamber. The nanostructures' sensing properties were tested in a wide range of operating temperatures towards ethanol and acetone.

3. Results and discussions

Morphological observations show that the well-aligned TiO_2 NTs with the homogeneous distribution over the substrates were obtained (Fig. 1 (a) and (b)). The micro-Raman spectrum of the sample annealed at 400 °C is reported in Fig. 1 (c). Structural investigations indicate that the NTs were crystallized in the anatase phase after the post-growth annealing at 400 °C for 6 h.

Fig. 2 (a) and (b) report conductometric sensing response of TiO_2 nanotubes towards ethanol and acetone. KP gas sensing analysis towards 10, 25 and 50 ppm of acetone at a working temperature of 400 °C are reported in Fig. 3.

The variations of the conductance and the work function of the samples shows that the n-type TiO_2 is the main phase in the nanotube structures indicating a reversible interaction between the nanotubes and the chemical species. The structures' response is quite high and the recovery of the signal is almost complete.

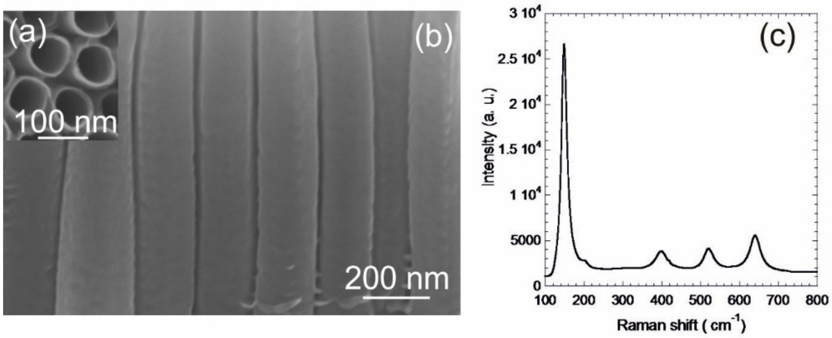

Fig. 1. SEM images of TiO_2 nanotube arrays. (a) Surface morphology of the nanotubes and (b) cross-section image of tubular arrays; (c) Raman spectrum of TiO_2 nanotubes. Spectrum was acquired using a 100X objective with laser excitation at 442 nm.

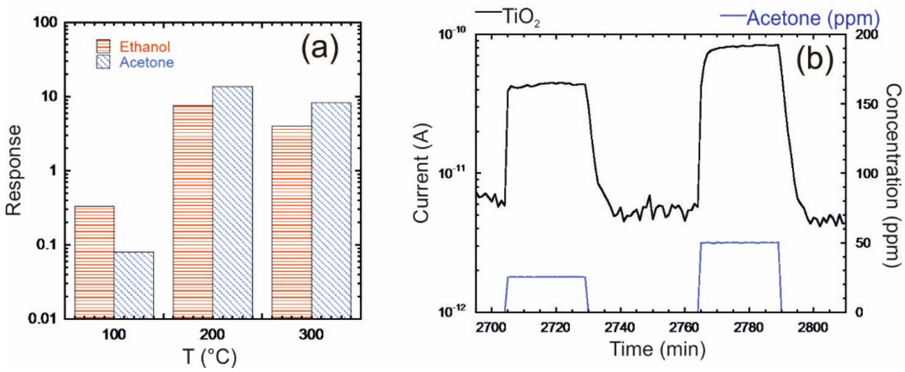

Fig. 2. (a) Response of TiO_2 nanotubes towards ethanol and acetone at 100 and 50 ppm, respectively, and working temperatures of 100, 200 and 300 °C; (b) dynamical response of TiO_2 nanotubes towards 25 and 50 ppm of acetone at a working temperature of 200 °C.

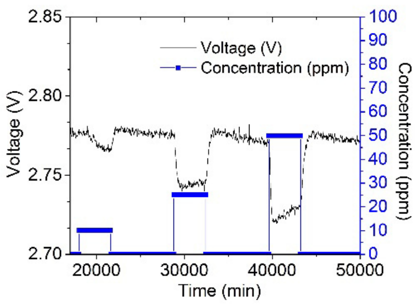

Fig. 3. KP acetone (10, 25 and 50 ppm) sensing response of TiO_2 nanotubes.

4. Conclusion

Highly ordered and well-aligned TiO_2 nanotube arrays have been obtained by means of anodization of metallic titanium films followed by post-growth annealing. The morphological and structural analysis showed that the prepared structures are TiO_2 NTs crystallized in the anatase phase. The obtained samples demonstrated high and reversible response to ethanol and acetone at high working temperatures. The preliminary results show that TiO_2 NTs are promising structures for the development of gas sensing devices and electronic noses.

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